CEMENT

AND

CEMENT MANUFACTURE

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Specification for Rapid-hardening Portland Cement.

THE means of distinguishing between ordinary and rapid-hardening Portland cements by specification tests and the drafting of a specification for rapidhardening Portland cement are problems that have been considered in many countries. Certain solutions have been presented, but in Great Britain, although a considerable amount of investigation has been done, no acceptable specification has yet been developed. A publication by the National Bureau of Standards of the U.S.A. (Research Paper R.P. 839) entitled "A Study for the Preparation of a Specification for High-Early-Strength Portland Cement" is therefore of great interest at the present time. Twenty-eight samples of commercial American high-early-strength Portland cements were examined and comprehensive chemical analyses and physical tests were made of each. A survey of the results shows how widely the cements under the common heading of "high early strength" varied in almost every particular. The proportions of tricalcium silicate calculated from the chemical analyses ranged from 44 to 74 per cent., but the former figure is not associated with the weakest cement nor the latter with the strongest. Similarly, no relation can be traced between strength and alumina content. Perhaps the most striking feature of the test results is the extreme fineness to which the cements have been ground, the average being 2,361 sq. cm. per gramme and the maximum 2,860 sq. cm. per gramme. The report states, quite truly, that for these cements the residue on the 200-mesh sieve means nothing. When the cement finenesses are compared with the strengths, however, there is again no clear relation, and it is evident that cement manufacturers in the United States at any rate have not confined themselves to any one direction in which to improve the quality of their normal cements so as to bring them into the category of rapid-hardening cements.

The most difficult problem in connection with a specification for rapid-

hardening cement, and indeed one that is connected with all cement specifications, is that of testing for strength. Broadly speaking it has not been easy to decide the most suitable proportion of water to be used for making the mortar briquettes or cubes, nor is it agreed that the more practical aspects of the compression tests justify the extra cost as compared with the old-established tensile tests. In Great Britain the impression is growing that the present method of testing, in which the minimum of water is used for gauging tensile briquettes, does not reveal the true concreting qualities of the cement. The United States investigators have been experimenting entirely with mortars of high water content, and arrive at the conclusions that the uniformity of strength of cubes in any one batch is better than that of briquettes, that no satisfactory method of determining the proportion of gauging water on a consistency basis is known, and that in default of this a system of fixed cement-water-ratio must be used. The mixture recommended is I part of cement to 2.77 parts of graded sand with a cement-water-ratio of 1.88. This is equivalent to more than 14 per cent. of water on the dry sand-cement mixture. The graded sand passes the 30-mesh sieve, 70 per cent. is retained on the 50-mesh sieve, and all is retained on the 100-mesh sieve. The suggested specification requirements for high-early-strength Portland cement with such a mortar are 1,300 and 3,000 lb. per square inch compressive strength at I and 3 days respectively. This method of testing seems to be the first step towards what would be welcomed by many, namely, a compression test of 6-in. cubes using sand and ballast with a water-cementratio similar to that which would apply in practical concreting under skilled supervision. The sensible suggestion is made that since 24-hour strength tests are to form a part of the specification it is unnecessary to specify a final setting

In the investigations on soundness, tests were made with bars of mortar 10 in. long which were cured in air, in steam at 100 deg. C., and in steam at 170 deg. C. respectively, with observations on length changes, and the conclusion is reached that the usual United States method of steaming a pat of neat cement does not call for any change at the present time.

Book Reviews.

[&]quot;Effect of Storage on the Properties of Cement." By Q. Sestini and L. Santarella. *Milan: Il Cemento Armato.*—This is a reprint, in the Italian language, of an article dealing with the effect on setting time, strength, and loss on ignition of storage of various types of cement in jute sacks, paper sacks, and hermetically-sealed iron packages.

[&]quot;RATIONAL USE OF PUMICE AS LIGHT-WEIGHT AGGREGATE." By Q. Sestini and L. Santarella. *Milan: L'Industria Italiana del Cemento.*—This is a reprint of an article, also in the Italian language, giving the results of tests showing the relations between strength, weight per unit volume, grading of aggregate and pozzolanic properties of concrete made with pumice aggregate.

Free Lime in Cement.*

The Ethylene Glycol and the Glycerol Methods.

By G. E. BESSEY, M.Sc., A.I.C., of the Building Research Station.

The determination of free lime in cements and other calcareous materials has been attempted in many ways. Hitherto the only method which has been widely used and considered satisfactory is the glycerol method originally suggested by Maynard¹ and developed by Emley² and by Lerch and Bogue.³ This method has been generally adopted for the determination of free lime in fresh cements, and the applicability of this and of some other methods has been discussed in a previous publication of the Building Research Station.⁴ In the meantime various new or modified methods have been proposed, and the present paper discusses the applicability of some modifications of the glycerol method, and of a similar method using ethylene glycol C₂H₄(OH)₂.

The Alcoholic-Glycerol Method (Lerch and Bogue).

A number of papers describing improvements or modifications of this method as applied to cements has appeared since the original paper by Lerch and Bogue. These authors described a revised procedure,⁵ and as a standard method this has generally been considered satisfactory. The time required for a determination has, however, led to suggestions for accelerating the method for works control purposes.

Meyers⁶ described an apparatus for three simultaneous titrations with mechanical agitation of the vessels containing the material; using this apparatus the method was stated to require 1½ to 3 hours for a determination.

Schläpfer and Bukowski¹⁰ carried out a comprehensive series of tests upon the rate of solution of calcium oxide and hydroxide in glycerol and alcoholic-glycerol at different temperatures, and found that the best results were obtained with a I:I alcohol-glycerol mixture, heated with continuous shaking for 20 minutes at 60 to 70 deg. C. followed by 10 minutes at 95 deg. C.; the temperature at which the alcohol-glycerol mix, used in the Lerch and Bogue method, boils is 80 to 85 deg. C. These authors obtained satisfactory results with this method but found that ethylene glycol was a more suitable solvent.

Brandenburg⁷ described a method of accelerating the rate of solution of the free lime by adding anhydrous barium chloride. This effect has been confirmed, and if certain precautions are taken the method is of value for routine testing. The barium chloride used is dehydrated by heating to constant weight at 150 to 250 deg. C. The procedure is similar to that in the normal method described by Lerch and Bogue except that 1 gm. of the barium chloride is added to the sample with the alcohol-glycerol mixture and the whole boiled rather more vigorously. The solution should be titrated at five-minute intervals. It has been found that there is first a rapid solution of the free lime, after which

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some of the other set cement compounds appear to be attacked causing a slow and continuous return of the colour of the indicator. This, if no allowance were made for it, would lead to high results for the free lime content. It is therefore necessary to use an arbitrary end-point, i.e., when less than o.r.c.c. of the ammonium acetate solution is required to remove the colour of the indicator after each of two consecutive five-minute intervals.† Using such an end-point for the titration, results agreeing with those by the normal method are obtained; the time taken for the determination is about one hour.

Garcia-Lorenzana⁸ has described a further modification of the method with a single titration after two hours, but no confirmatory tests of the accuracy of the results given by this modification are available.

The Pure Glycerol Method.

The modifications¹ of Maynard's original method, in which the sample is heated with glycerol alone, have not proved to be so generally applicable as the alcoholic glycerol method. It has been found that there is some attack of tricalcium silicate by the glycerol when used alone, and that this method therefore tends to give high results.⁴ The modification described by the writer⁵ has, however, been used satisfactorily for sand-lime bricks.

The Ethylene-Glycol Method (Schläpfer and Bukowski).

Comparative tests of the rate of solution of lime (calcium oxide and hydroxide) in glycerol [C₃H₅(OH)₃] and ethylene glycol [C₂H₄(OH)₂] were made by Schläpfer and Bukowski, 10 and they conclude that the glycol is preferable to glycerol as a solvent for extracting free lime. As applied to cements, their method, which requires an oil or water bath fitted with a shaking device, is as follows. The sample of cement or ground clinker, weighing 0.5 to 1.0 gm., is placed in a small dry flask with 40 ml. of ethylene glycol and a pinch of clean quartz grains to assist in preventing caking. The flask is closed with a rubber bung and shaken in a water bath at 65 to 70 deg. for 30 minutes. The flask is then removed from the bath and the solution filtered through a Jena sintered-glass filter (3G3) or through hardened paper on a porcelain plate. The residue in the flask and on the filter is washed three times with about 10 ml. of absolute alcohol and titrated with o.I normal alcoholic benzoic acid solution or o.I normal aqueous hydrochloric acid solution. With light coloured, sulphide-free, materials the solution can be titrated directly without filtration, but it is preferable to filter in all cases to maintain standardised conditions. The indicator which was found most suitable was a mixture of 0.10 gm. phenolphthalein with 0.15 gm. a-naphtholphthalein dissolved in 100 ml. of absolute alcohol. The ethylene glycol must be pure, neutral, and free from water. The neutrality towards the indicator should be tested, and the density should be 1.100 gm. per ml. at 20 deg. C. The alcohol used by Schläpfer and Bukowski for preparing the benzoic acid solution and for washing the filter was ethyl alcohol containing 5 per cent. methyl alcohol, redistilled over lime to remove traces of water.

[†] Private communication from Messrs. Casebourne & Co. (1926), Ltd.

Applicability of Method.

(a) CEMENTS.—This method is stated by Schläpfer and Bukowski to be applicable to cements, slags, set cements and sand-lime bricks. In work carried out at the Building Research Station on cements and cement clinker it has been found to give satisfactory results, agreeing with the Lerch and Bogue glycerol method.

In Table I are shown the total free lime contents of a number of cements and clinkers determined by both methods together with free calcium hydroxide contents by the Loss method. In most cases the results given are the mean of two or more determinations; the reproducibility of results by the glycol method was found to be at least as good as that of the alcoholic-glycerol method. The method is found to be equally applicable whether the free lime in the cement is present as oxide or hydroxide.

TABLE I.
Free Lime Contents of Cements and Clinkers.

Sample				Total fr	Calcium hydroxide	
No.			Ethylene glycol method (CaO%).	Glycerol method (CaO%).	by Loss method (CaO%).	
Cement	I			3.9	4-3	3.6
11	2			1.7	1.7	1.5
**	3			2.9	2.9	2.2
**	4			0.8	0.6	1.0
**	5			2.I	2.5	2.1
	6			4.7	4.9	4.4
**	7			0.4	0.4	Nil
3.2	8			0.3	0.3	0.2
Clinker	I			2.4	2.7	
	2			2.5	2.4	
12	3			1.0	0.8	
1.6	4			2.7	2.7	
21	5			0.5	0.4	
* *	6			4.4	4.4	

It has been found that if the solution is filtered, absolute alcohol need not be used for washing; the use of ordinary industrial methylated spirit is satisfactory for routine purposes provided it is neutral in reaction and the filtration and washing are carried out rapidly. If methylated spirit is used, followed by titration with aqueous hydrochloric acid, the cost of the reagents is less and the used solution may be discarded. The agitation must be continuous and vigorous to give satisfactory results with a heating period of 30 minutes. Either an oil or water bath fitted with a suitable shaker, and preferably thermostatic control, is suitable. Sintered glass filters should be used only once and then washed with hydrochloric acid, followed by sodium carbonate and distilled water; several may be washed together to save time and cleaning solutions.

(b) HYDRATED MATERIALS.—The method has not been found satisfactory for set cements. There is at present no absolute reference method with which results may be compared, and the only means of judging the suitability of a

proposed method for the determination in a set cement are the reproducibility of the results and tests on such of the compounds existing in set cement as are available.

Schläpfer and Bukowski state that with the given procedure calcium hydroxide is completely dissolved. This has been confirmed for the fine grained or amorphous calcium hydroxide formed by direct hydration of calcium oxide by water, but it has been found that crystalline calcium hydroxide does not dissolve readily. A sample of well-crystallised hydroxide was prepared by boiling a saturated solution of lime, and found by optical examination to be pure except for traces of carbonate. Separate portions of this were ground to pass a 170-mesh B.S. sieve and to flour fineness (maximum particle size, 35μ diameter), and tested according to the procedure described.

Only 24 and 32 to 36 per cent. CaO respectively was found instead of the 75 per cent. calculated. These results, together with those for the amorphous material, are shown in Table II. If allowed to stand the colour of the indicator

TABLE II.
SOLUTION OF CALCIUM HYDROXIDE IN ETHYLENE GLYCOL.

Sample.	Weight of sample (gm.).	Calculated free CaO content (per cent.).	Free CaO by glycol method (per cent.).	
Amorphous calcium hydroxide {	0.064	72 72	71 73	
Crystalline calcium hydroxide: (1) Through 170-mesh (2) Flour fineness	0.061 0.068 0.043	75 75 75	24 32 36	

continually returned owing to further slow solution of the lime; in one sample showing 32 per cent. free lime after the normal half-hour period, the total amount found after standing for several hours with occasional titration was 45 per cent.

It is known that a portion at least of the free lime in a set cement is present as crystals of appreciable size; it may be inferred therefore that low results may be obtained as result of this difficulty of dissolving the crystalline material. This is in some degree confirmed by observations made during actual determinations on mortars; it is difficult in some cases to obtain a definite end point owing to the slow return of the indicator colour. On some neat set cement samples tested at early ages, on the other hand, the end-point was reasonably sharp. It is possible that in these latter cases the calcium hydroxide had not formed crystals of appreciable size.

Schläpfer and Esenwein¹² have recently published a paper describing further work on the method in relation to its applicability to hydrated materials. They have tested the effect of the solvent upon certain of the hydrated calcium aluminates and calcium sulpho-aluminate and have found that there is comparatively little decomposition of the cubic compound 3CaO.Al₂O₃.6H₂O, but that both the di- and tetra-calcium aluminates (hexagonal plate crystals) and calcium sulpho-aluminate are very appreciably attacked.

Assuming the alumina in set cements to be present as tetra-calcium aluminate and sulpho-aluminate, it would appear from their results that the free lime value obtained may, on account of partial decomposition of these compounds, be as much as 2.5 per cent. CaO too high.

The constitution of the hydrated calcium silicate gels occurring in set cement is at present being investigated, but this work is not yet sufficiently advanced to give any definite indication of the action of ethylene glycol upon individual compounds; it would appear, however, from such tests as have so far been carried out that the hydrated silicates occurring in set cement also suffer some degree of attack by this solvent.

These considerations show that the ethylene glycol method cannot be considered satisfactory for set cements. The incomplete solution of calcium hydroxide when in a well-crystallised state results in low values, whilst attack of other hydrated cement compounds tends to give high results. These opposing errors may tend to cancel out to some degree, but there is no means of determining how far this may be the case. In comparative tests on hydrated cements up to 28 days old the glycol method gives the highest values for free lime content, the calorimetric method¹³ gives the lowest values, and intermediate values are generally obtained by extraction in lime-water to a final concentration approaching saturation. Examples of the results obtained for neat cements at ages of 7 and 28 days are shown in Table III.

TABLE III.
FREE LIME IN SET CEMENT BY DIFFERENT METHODS.

	Free	lime (as CaO per o	cent.).
Sample.	By glycol method.	By calorimetric method.	By lime solution extraction method.*
Normal Portland :		+	
Neat. Water stored 7 days	10.2	4.9	10.9
,, 28 days	11.7	5.9	11.0
Rapid-hardening Portland:			
Neat. Water stored 7 days	16.4	7.8	12.0
,, ,, ,, 28 days	10.4	7.4	11.3

The final concentration of the lime solution in this test was between 0.094 and 0.099 gm. per 100 ml.; the value so obtained is considered to be higher than the true free lime content, as some hydrolysis and further hydration of the cement probably occur.

In these cases the results obtained by the glycol method appear to be high; at later ages the formation of larger crystals of calcium hydroxide may tend to increase the negative error. The results obtained by Rodt¹⁴ who finds a decreasing free lime content in Portland cement when stored in water in the absence of carbon dioxide, may possibly be attributed to this effect.

Conclusions.

For the determination of free lime in cements the alcoholic-glycerol method of Lerch and Bogue is, in respect of accuracy, probably the most satisfactory

method and it is widely used. It is, however, somewhat tedious for routine purposes and more rapid methods are desirable.

Two other methods have been found to give satisfactory results for such purposes. The accelerated alcoholic-glycerol method suggested by Brandenburg is satisfactory provided that certain precautions and an arbitrary end-point are taken. The ethylene-glycol method of Schläpfer and Bukowski is satisfactory and rapid.

The ethylene-glycol method has not been found to be satisfactory with hydrated cements, as crystalline calcium hydroxide dissolves with difficulty tending to make the result low, while other hydrated cement compounds are attacked thus tending to give a high result.

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Cooling of Clinker. By F. Lipinski. (Tonind. Zeit., 1935, pp. 333, 354). The author points out the saving in heat, equivalent to 16.7 per cent. of the coal used, which can be obtained by using an efficient clinker cooler where the combustion air is heated before admission to the kiln. Various types of cooler, such as stationary shaft coolers, rotating coolers, and integral coolers, are described in detail and discussed. It is pointed out that actually more than 16.7 per cent. saving can be made by an efficient cooler because, since less coal is used, a smaller amount of combustion air is required, giving a smaller amount of flue gas and therefore less possibility of loss of heat. The conditions in the kiln improve and a large output can be maintained, which gives a lower radiation loss per unit weight of clinker.

Specific Heat of Rotary Kiln Gases at Constant Pressure.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

The specific heat of a gas is the ratio of the quantity of heat required to raise the temperature of the gas one degree to that required to raise the temperature of an equal mass of water one degree—usually from 14.5 deg. C. to 15.5 deg. C. Since the specific heat is a ratio, it is of the same magnitude whether it is expressed in metric units (calories per gramme per degree Centigrade) or in British units (British Thermal Units per pound per degree Fahrenheit).

For calculations in connection with rotary kiln gases only the specific heat at constant atmospheric pressure is required. There are four specific heat tables commonly required in thermal calculations, namely:

True or instantaneous specific heat:

(1) in B.T.U.s per pound of gas per degree Fahrenheit.

(2) in B.T.U.s per cubic foot of gas at N.T.P. per degree Fahrenheit.

Mean specific heat between 32 deg. F. and T deg. F.:

(3) in B.T.U.s per pound of gas per degree Fahrenheit.

(4) in B.T.U.s per cubic foot of gas at N.T.P. per degree Fahrenheit.

Many determinations of specific heats of gases have been made, but the results are very conflicting. For this reason it has been considered advisable, in the tables given on the following pages, to take the calculated values of Justi and Lüder (Forschung Ingenieurwesen, Sept.—Oct., 1935, 6) which are based on the spectroscopic characteristics of the gases. The values for mean specific heats of gases given therein agree closely with those of F. Habert (Warmetechnische Tabellen, Verlag Stahleisen, m.b.H. Dusseldorf, 1935, lfd. Blatt 117). The values for sulphur dioxide have been calculated from the formula given by Halferdahl (Chem. & Met. Eng., 1930, 37, p. 686).

(See tables on pages 170 to 173).

New Method of Determining Setting Time. By S. Solacolu. (Tonind. Zeil., 1935, p. 846).—The absorption of water in a cement pat causes a vacuum between the grains of cement (and sand if it is present) which presses the plastic mass on to the grains and causes it to adhere to them. When the maximum amount of water has been absorbed the vacuum is destroyed and the pressure rises. It is suggested that the setting time should be taken as the time when this occurs. The suggested apparatus for measuring the setting time consists of a funnel to the lower end of which a U-tube filled with petroleum is fixed. To the upper portion of the funnel a mould is fixed by screws. The base of the mould consists of a perforated plate, and a rubber ring is used to make it airtight. The portion of the mould above the perforated plate is filled with cement paste. As setting proceeds a partial vacuum is formed below the perforated plate and the level of the petroleum in the U-tube changes. At first there is a drop in pressure and then a sharp rise. The setting time is taken as the time when the rise commences.

TABLE I. Instantaneous Specific Heat of Rotary Kiln Gases at Constant Atmospheric Pressure. [Cal. per gm. of gas per deg. C. or B.T.U.s per lb. of gas per deg. F.]

Deg. F.	Deg. C.	Oxygen.	Nitrogen.	Air.	Carbon monoxide.	Carbon dioxide.	Steam.	Sulphur
32	0	0.2184	0.2476	0.2396	0.2488	0.1955	0.4429	0.1420
212	100	0.2226	0.2482	0.2414	0.2496	0.2198	0.4491	0.1494
300	149	0.2257	0.2492	0.2430	0.2507	0.2288	0.4550	0.1528
400	204	0.2300	0.2506	0.2450	0.2525	0.2388	0.4620	0.1567
500	260	0.2352	0.2526	0.2475	0.2551	0.2487	0.4680	0.1606
600	315	0.2395	0.2550	0.2504	0.2584	0.2572	0.4770	0.1644
700	371	0.2433	0.2577	0.2535	0.2618	0.2647	0.4855	0.1680
800	426	0.2467	0.2606	0.2567	0.2656	0.2710	0.4950	0.1716
900	482	0.2497	0.2640	0.2600	0.2693	0.2770	0.5030	0.1751
1,000	538	0.2526	0.2675	0.2631	0.2728	0.2823	0.5130	0.1786
1,100	594	0.2553	0.2705	0.2670	0.2761	0.2870	0.5230	0.1817
1,200	649	0.2577	0.2736	0.2687	0.2794	0.2912	0.5325	0.1850
1,300	704	0.2597	0.2764	0.2714	0.2820	0.2948	0.5425	0.1883
1,400	760	0.2617	0.2792	0.2740	0.2847	0.2980	0.5520	0.1914
1,500	815	0.2636	0.2817	0.2754	0.2874	0.3008	0.5600	0.1946
1,600	871	0.2652	0.2840	0.2787	0.2897	0.3035	0.5680	0.1976
1,700	927	0.2667	0.2865	0.2806	0.2920	0.3060	0.5775	0.2004
1,800	982	0.2681	0.2885	0.2824	0.2940	0.3080	0.5850	0.2030
1,900	1,038	0.2694	0.2907	0.2843	0.2958	0.3103	0.5940	0.2057
2,000	1,093	0.2704	0.2924	0.2859	0.2975	0.3120	0.6020	0.2084
2,100	1,148	0.2716	0.2942	0.2863	0.2992	0.3140	0.6080	0.2109
2,200	1,204	0.2727	0.2956	0.2887	0.3004	0.3155	0.6160	0.2133
2,300	1,261	0.2737	0.2970	0.2899	0.3017	0.3170	0.6225	0.2157
2,400	1,316	0.2747	0.2983	0.2911	0.3028	0.3180	0.6280	0.2181
2,500	1,372	0.2756	0.2994	0.2922	0.3038	0.3190	0.6360	0.2203
2,600	1,427	0.2766	0.3004	0.2932	0.3047	0.3200	0.6425	0.2225
2,700	1,483	0.2776	0.3014	0.2943	0.3056	0.3210	0.6480	0.2247

TABLE 2.

Instantaneous Specific Heat of Rotary Kiln Gases at Constant Atmospheric Pressure.

[B.T.U.s per deg. F. for gas occupying 1 cub. ft. at N.T.P.]

Deg. F.	Deg. C.	Oxygen.	Nitrogen.	Air.	Carbon monoxide.	Carbon dioxide.	Steam.	Sulphur dioxide.
32	0	0.01950	0.01940	0.01940	0.01940	0.02400	0.02220	0.02530
212	100	0.01990	0.01947	0.01954	0.01950	0.02700	0.02250	0.02660
300	149	0.02016	0.01956	0.01966	0.01960	0.02810	0.02275	0.02720
400	204	0.02053	0.01970	0.01983	0.01975	0.02930	0.02307	0.02790
500	260	0.02096	0.01987	0.02003	0.01996	0.03050	0.02348	0.0286
600	315	0.02130	0.02004	0.02025	0.02024	0.03150	0.02392	0.02932
700	371	0.02163	0.02024	0.02049	0.02052	0.03235	0.02436	0.03000
800	426	0.02195	0.02046	0.02074	0.02079	0.03315	0.02480	0.03065
900	482	0.02223	0.02069	0.02102	0.02105	0.03390	0.02525	0.03130
1,000	538	0.02253	0.02094	0.02125	0.02131	0.03456	0.02572	0.03192
1,100	594	0.02277	0.02117	0.02149	0.02156	0.03514	0.02617	0.03250
1.200	649	0.02297	0.02145	0.02171	0.02182	0.03566	0.02665	0.03310
1,300	704	0.02316	0.02168	0.02193	0.02205	0.03608	0.02707	0.03368
1,400	760	0.02334	0.02187	0.02213	0.02226	0.03650	0.02754	0.03426
1,500	815	0.02350	0.02203	0.02232	0.02246	0.03690	0.02802	0.03484
1,600	871	0.02366	0.02218	0.02250	0.02264	0.03724	0.02847	0.03535
1,700	927	0.02380	0.02241	0.02267	0.02281	0.03755	0.02890	0.03582
1,800	982	0.02393	0.02264	0.02282	0.02295	0.03784	0.02933	0.03628
1,900	1,038	0.02404	0.02284	0.02296	0.02309	0.03808	0.02977	0.03674
2,000	1,093	0.02414	0.02297	0.02308	0.02323	0.03832	0.03015	0.03720
2,100	1,148	0.02424	0.02309	0.02322	0.02334	0.03854	0.03051	0.03765
2,200	1,204	0.02434	0.02318	0.02333	0.02344	0.03874	0.03086	0.03806
2,300	1,261	0.02444	0.02325	0.02345	0.02356	0.03889	0.03122	0.03850
2,400	1,316	0.02453	0.02333	0.02355	0.02365	0.03903	0.03155	0.03894
2,500	1,372	0.02462	0.02342	0.02364	0.02374	0.03915	0.03187	0.03934
2,600	1,427	0.02471	0.02354	0.02373	0.02382	0.03927	0.03219	0.03974
2,700	1,483	0.02478	0.02366	0.02381	0.02389	0.03938	0.03253	0.04013

TABLE 3.

MEAN SPECIFIC HEAT OF ROTARY KILN GASES AT CONSTANT ATMOSPHERIC PRESSURE BETWEEN 32 DEG. F. (0 DEG. C.) AND TEMPERATURES GIVEN IN COLS. I AND 2.

[Cal. per gm. of gas per deg. C. or B.T.U.s per lb. of gas per deg. F.]

Deg. F.	Deg. C.	Oxygen.	Nitrogen.	Air.	Carbon monoxide.	Carbon dioxide.	Steam.	Sulphur
32	0	0.2184	0.2476	0.2396	0.2488	0.1955	0.4429	0.1420
212	100	0.2205	0.2476	0.2403	0.2489	0.2082	0.4454	0.1457
300	149	0.2217	0.2478	0.2410	0.2490	0.2137	0.4477	0.1476
400	204	0.2234	0.2484	0.2419	0.2494	0.2196	0.4505	0.1495
500	260	0.2254	0.2493	0.2429	0.2502	0.2248	0.4540	0.1514
600	315	0.2274	0.2501	0.2440	0.2513	0.2298	0.4574	0.1535
700	371	0.2294	0.2511	0.2453	0.2529	0.2343	0.4610	0.1556
800	426	0.2313	0.2522	0.2466	0.2544	0.2386	0.4647	0.1576
900	482	0.2333	0.2534	0.2478	0.2557	0.2426	0.4690	0.1594
1,000	538	0.2353	0.2546	0.2491	0.2574	0.2465	0.4730	0.1611
1,100	594	0.2361	0.2559	0.2503	0.2588	0.2502	0.4774	0.1627
1,200	649	0.2387	0.2572	0.2517	0.2603	0.2537	0.4812	0.1644
1,300	704	0.2402	0.2586	0.2532	0.2624	0.2570	0.4856	0.1661
1,400	760	0.2416	0.2599	0.2546	0.2642	0.2597	0.4904	0.1679
1,500	815	0.2430	0.2613	0.2561	0.2660	0.2624	0.4953	0.1697
1,600	871	0.2443	0.2627	0.2574	0.2674	0.2647	0.4994	0.1713
1,700	927	0.2456	0.2642	0.2587	0.2687	0.2671	0.5040	0.1731
1,800	982	0.2467	0.2656	0.2600	0.2699	0.2693	0.5084	0.1747
1,900	τ,038	0.2482	0.2669	0.2614	0.2711	0.2713	0.5124	0.1764
2,000	1,093	0.2493	0.2682	0.2627	0.2723	0.2733	0.5163	0.1777
2,100	1,148	0.2504	0.2694	0.2640	0.2735	0.2753	0.5197	0.1794
2,200	1,204	0.2513	0.2705	0.2650	0.2747	0.2772	0.5232	0.1807
2,300	1,261	0.2524	0.2717	0.2660	0.2759	0.2790	0.5278	0.1823
2,400	1,316	0.2535	0.2728	0.2668	0.2770	0.2807	0.4325	0.1836
2,500	1,372	0.2544	0.2740	0.2677	0.2780	0.2823	0.5375	0.1851
2,600	1,427	0.2553	0.2750	0.2688	0.2789	0.2836	0.5417	0.1874
2,700	1,483	0.2562	0.2760	0.2702	0.2797	0.2847	0.5453	0.1896

TABLE 4.

MEAN SPECIFIC HEAT OF ROTARY KILN GASES AT CONSTANT ATMOSPHERIC PRESSURE BETWEEN 32 DEG. F. (0 DEG. C.) AND TEMPERATURES GIVEN IN COLS. I AND 2.

[B.T.U.s per deg. F. for gas occupying 1 cub. ft. at N.T.P.]

Deg. F.	Deg. C.	Oxygen.	Nitrogen.	Air.	Carbon monoxide.	Carbon dioxide.	Steam.	Sulphur dioxide.
32	0	0.01950	0.01940	0.01941	0.01940	0.02400	0.02220	0.02530
212	100	0.01960	0.01942	0.01943	0.01942	0.02550	0.02234	0.02600
300	149	0.01970	0.01944	0.01945	0.01945	0.02624	0.02246	0.02630
400	204	0.01990	0.01949	0.01952	0.01950	0.02694	0.02261	0.0266
500	260	0.02008	0.01953	0.01959	0.01955	0.02758	0.02277	0.0270
600	315	0.02027	0.01960	0.01967	0.01961	0.02817	0.02294	0.02740
700	371	0.02045	0.01968	0.01976	0.01970	0.02875	0.02313	0.02774
800	426	0.02062	0.01978	0.01985	0.01979	0.02933	0.02333	0.02810
900	482	0.02078	0.01989	0.01994	0.01991	0.02982	0.02354	0.02842
1,000	538	0.02095	0.02000	0.02005	0.02004	0.03027	0.02377	0.02875
1,100	594	0.02111	0.02009	0.02017	0.02018	0.03068	0.02397	0.02906
1,200	649	0.02126	0.02021	0.02033	0.02034	0.03106	0.02419	0.02938
1,300	704	0.02142	0.02031	0.02047	0.02049	0.03143	0.02442	0.02970
1,400	760	0.02155	0.02042	0.02059	0.02062	0.03185	0.02467	0.03000
1,500	815	0.02168	0.02052	0.02068	0.02073	0.03213	0.02490	0.03031
1,600	871	0.02180	0.02061	0.02078	0.02085	0.03244	0.02511	0.03061
1,700	927	0.02190	0.02070	0.02087	0.02097	0.03275	0.02536	0.03093
1,800	982	0.02198	0.02080	0.02097	0.02108	0.03301	0.02557	0.03121
1,900	1,038	0.02207	0.02089	0.02106	0.02119	0.03327	0.02578	0.03150
2,000	1,093	0.02216	0.02098	0.02116	0.02129	0.03355	0.02599	0.03178
2,100	1,148	0.02226	0.02107	0.02127	0.02137	0.03378	0.02618	0.03204
2,200	1,204	0.02236	0.02118	0.02137	0.02146	0.03401	0.02639	0.03234
2,300	1,261	0.02246	0.02129	0.02147	0.02154	0.03422	0.02660	0.03260
2,400	1,316	0.02256	0.02139	0.02157	0.02163	0.03442	0.02680	0.03286
2,500	1,372	0.02266	0.02149	0.02167	0.02171	0.03461	0.02700	0.03308
2,600	1,427	0.02276	0.02158	0.02177	0.02179	0.03480	0.02718	0.03342
2,700	1,483	0.02286	0.02168	0.02187	0.02187	0.03496	0.02736	0.03383



Fig. 1.

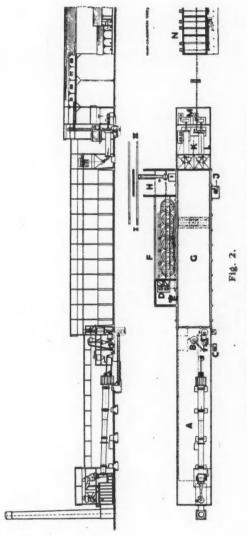
A Modern Cement Works with Concentra Rotary Kiln and Concentrator.

By DR. G. RUPPERT.

A LARGE lime works on the Continent with available raw materials which were also suitable for the manufacture of Portland cement has now erected a Portland cement factory adjacent to the lime works. The supply of the mechanical equipment for the new undertaking was entrusted to the Krupp-Grusonwerk.

Rotary-kiln and shaft-kiln burning tests carried out by Krupp-Grusonwerk with samples of the raw materials showed very high cement strengths, especially in the case of the rotary-kiln cement, and it was decided to install a wet-process rotary-kiln plant and Concentrator. It was found that the existing mechanical and electrical shops could also be used in connection with the cement plant, and that some of the large lime silos could be used as cement silos, and the cost of new buildings thereby kept down. A general view of the new plant is given in Fig. 1 and a plan in Fig. 2. The cement factory is alongside the existing railway siding.

Each section of the plant may be enlarged by the provision of additional equipment without interrupting the working of the installation as a whole. All machines with high power consumption are of large size so that they need only be operated during eight hours at night in order to take advantage of a lower price for electricity. The kiln runs day and night, whereas work in the quarry and in the primary crushing plant is by day only. Raw material is blasted at the quarry and loaded into tip wagons which are hauled to the crushing plant at the cement works by a loco. The material is tipped on to an inclined conveyor belt which delivers it to a hammer breaker wherein it is broken into pieces averaging 1 16 in. to 1 16 in. in size and delivered by a bucket elevator to the raw material store. In this building, in which the clinker is also stored, there is a travelling grab hoist of nearly 2 cb. yd. capacity, which is used for feeding the mill and gypsum stock bins and also for distributing the clinker.



A—Kiln house; B—Coal mill; C—Firing; D—Slurry pumps; E—Compressor; F—Slurry silos; G—Clinker store; H—Raw material, primary reduction;

L-Cement mill;

J-Gypsum, primary reduction; K-Slurry mill; M-Motor room, mill drive; N-Cement silos.

r room, mill grave; N.--Cement slios.

I = from quarry I; II = from quarry II.

From the raw-material dump the primary-crushed rock is delivered to a Krupp-Grusonwerk slurry mill by two plate feeders. This mill is 7 ft. $10\frac{1}{2}$ in. diameter and about 39 ft. $4\frac{1}{2}$ in. long, and incorporates the patented Krupp Concentra device and Krupp Centra drive. The two-stage reduction gear employed in the Centra drive maintains constantly an efficiency of 98 per cent. Figs. 3 and 5 show the substantial construction of the mill and the separately-housed totally-enclosed driving gear. The Concentra device (Fig. 4) also contributes to efficiency and economy in that the driving power required is extremely low. For example, for an output of 29 to 30 tons and a fineness of 7 to 8 per cent.

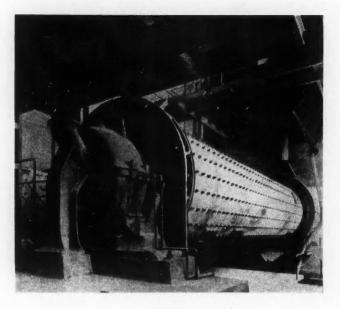


Fig. 3.

residue on the 4,900-mesh sieve, the mill requires 540 h.p., which is equivalent to approximately 12.8 kW. per ton.

Above the slurry mill is a water tank which is kept filled by an automatically-controlled pump, and under the mill the slurry, with a water-content of 38 to 40 per cent., is collected in a pit from which it is pumped to the slurry tanks, of which there are six measuring about 18 ft. diameter by 46 ft. high and having a capacity of 392 cb. yd. The total charge when all the tanks are full is sufficient for six days operation of the kiln.

Air is forced into the slurry tanks separately at night by a 40-h.p. compressor, delivering about 424 cu. ft. per minute at 29 to 44 lb. per square inch above atmos-

pheric pressure to agitate the contents of each tank. The air supply to the tanks is controlled mechanically by valves automatically operated by a slowly-rotating camshaft. Only one valve is open at a time, so that the full supply of air is admitted to each tank separately. As the raw material has little tendency to



Fig. 4

settlement, the compressor is operated for two or three hours only on each occasion in order to balance or make up the slurry in these tanks. The tanks have inclined bottoms, but settlement is prevented by taking the air pipes to the bottom. Discharge pipes with valves are connected at the base of each tank.

The mixed slurry is conducted at a variable rate to a sump having two compartments, from one of which the slurry is delivered to the kiln inlet by means of a centrifugal pump, while the other compartment, which is also connected to a

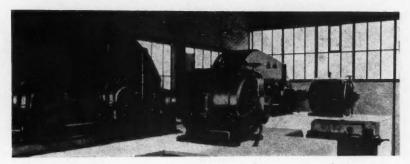


Fig. 5.

pump, is reserved for the slurry necessary for making up or balancing the contents of the six tanks. Both pumps have easily-renewable wear-resisting gears and casing, and they are interconnected by pipes so that each can be used if desired for both kiln feeding and slurry pumping (Fig. 6).

Measuring of slurry is by a variable-speed elevator at the inlet end of the kiln above the Concentrator. This elevator is driven by a motor, the speed of which is electrically controlled by the speed of the kiln rotation, so that interruptions in burning due to faulty feeding are avoided.

The kiln (Fig. 7) has a diameter 7 ft. $4\frac{5}{8}$ in. at the inlet end and just over 9 ft. at the outlet end and a total length of nearly 148 ft. It is slightly inclined and makes 1 to $1\frac{1}{2}$ revolutions a minute. In the Concentrator, through which the slurry passes immediately before entering the kiln, the water content is reduced to 12 to 14 per cent. by contact with the waste gases from the kiln. The elevator delivers the slurry in measured quantities into a tank above the Concentrator,

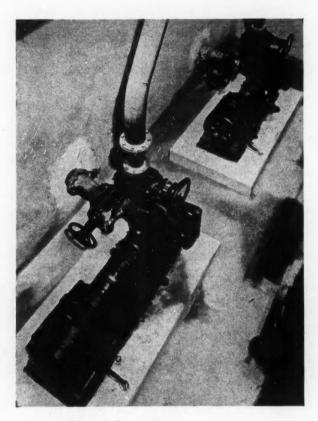


Fig. 6.

from which it passes through nozzles, which open and close alternately, as a continuous stream into the Concentrator.

The Concentrator consists of a grate-drum charged with heat-exchanging media over which the slurry spreads and is quickly dried by the hot waste gases coming upward from the kiln through the grate in the drum. The slurry, when it is dried on the filling media, is detached therefrom by their repeated collisions

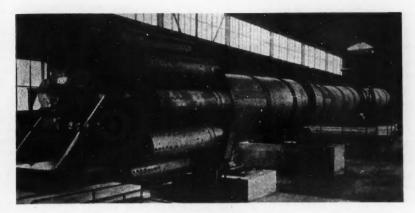


Fig. 7.

with one another under the action of the rotating drum and falls, in the form of pellets, through the grate and so into the kiln.

The waste gases from the kiln have a temperature of about 820 deg. C., and after passing through the Concentrator their temperature is 100 to 120 deg. C. The gases then pass through a duplex cyclone dust-precipitation device, and are white when they leave the chimney.

Arranged circumferentially around the outlet end of the kiln are the drums

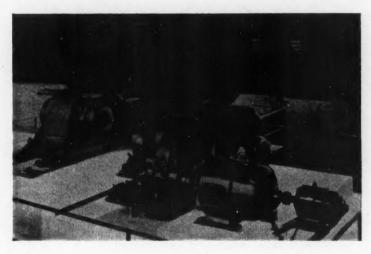


Fig. 8.

of the Concentra cooler in which, by being constantly turned over and lifted, the hot clinker is cooled to a temperature of about 100 to 150 deg. C.

A variable-speed motor coupled to a completely-enclosed three-stage reduction gear running in oil (Fig. 8) rotates the kiln. Only two men are necessary to look after the kiln and slurry-pumping plant. All controls are arranged so that without leaving his position the man in charge of the burning can regulate the speeds of the slurry feed, Concentrator, waste-gas blower, kiln, coal fan, and coal feed.

Kiln fuel is composed of Upper Silesian and Ruhr coal, in equal proportions, delivered from the storage bunker by a plate feeder to a Krupp Universal grinding and drying mill 6 ft. 6\frac{3}{4} in. diameter by 6 ft. 6\frac{3}{4} in. long (Fig. 9) in which it is ground and, by the hot air blown in, simultaneously dried. By this method separate



Fig. 9.

drying drums and conveyor equipment are dispensed with. The output of the plant, taking the moisture-content of the raw coal at 8 to 10 per cent., is 3.8 tons hourly with 8 to 10 per cent. residue on the 4,900-mesh sieve. The mill, the fan and the filter have a total power consumption of 132 h.p., and are operated during the cheap current period.

The output of the burning plant was guaranteed to be not less than 130 to 135 tons per twenty-four hours with a coal consumption of about 5,555 B.T.U. per kg. of clinker. Tests when the plant was taken over showed the output to be 145 tons and the coal consumption 18.42 per cent. As the calorific value of the coal used was 12,931 B.T.U., the heat consumption amounted to about 5,254 B.T.U. per kg. of clinker. The total power required by the kiln plant is

87 h.p., of which 35 h.p. is used by the waste-gas fan, 12 h.p. by the Concentrator, 25 h.p. by the kiln, and 15 h.p. by the pulverised coal fan.

The burnt clinker, which has a fine-grained, sharp-burned structure of a dark colour, is delivered to the clinker store by conveyor belt and elevator after being automatically weighed. From this store the crane takes the clinker to the storage bunker above the cement mill; the crane also feeds the gypsum into a separate container in front of the mill.

The cement mill has the same dimensions as the slurry mill; it is also of similar design and is equipped with the internal Concentra device. It is claimed that a cement output of 19.5 tons hourly with a fineness of 7 to 8 per cent. residue on the 4,900-mesh sieve and a power consumption of 570 h.p. could be assured. As the internal Concentra device results in powerful draught through the mill, the cement is discharged with a very low temperature and does not require lengthy seasoning; also, the disadvantage of the water-content being driven out of the gypsum giving rise to quick sets is avoided.

Like the slurry mill, the cement mill is driven by a 680-h.p. motor through an enclosed reduction gear. A large hose filter is connected to the mill to ensure dust-free operation. A Redler conveyor nearly 197 ft. long takes the finished cement to the silos, from which it is drawn and, by means of an automatic Haver and Böcker packing machine, packed ready for transport. All driving motors and associated electrical equipment were supplied by Messrs. Brown, Boveri A.-G.

The raw materials used are limestone and marl. The composition of the finished cement is: SiO_2 , 20.39 per cent.; Al_2O_3 , 7.43 per cent.; Fe_2O_3 , 3.45 per cent.; CaO, 63.94 per cent.; MgO, r.98 per cent.; SO_3 , r.98 per cent.

Tests of the cement have given the following results:

		Tensile.		Compression.		
Days	3	7	28	3	7	28
Strength (kg. per sq. cm.)	36.65	54.26 .	65.73	172.7	293.6	369
Allowable minimum (usual Standards) less tolerance	-	31.5	40.5	_	162	247.5

Vertical Illumination in Examining Clinker Sections. By E. Spohn. (Tonind. Zeit., 1935, p. 849).—The examination of polished clinker surfaces by reflected light under the microscope is suggested as an important help in the examination of Portland cement in addition to the examination of thin sections by transmitted light. The advantages claimed are a clearer picture, sharper contours to the mineral grains which assist in quantitative estimations, and ease and speed of preparation of specimens. Specially-prepared specimens can be examined either by reflected or transmitted light. The main result of the tests showed that clinkers consist chiefly of 3CaO.SiO₂ embedded in a structureless ground-mass which must be considered a glass. The paper is illustrated with photographs taken both by reflected and by transmitted light.

Abstracts from the Foreign Press.

Production of Portland Cement in a Blastfurnace. By G. Mussgnug (Tonindustrie Zeitung, 1935, pp. 775, 789, 803).—The production of Portland cement and iron in a blastfurnace was the subject of experiments using a slag of the composition of Portland cement and an oxygen-enriched air blast to obtain the necessary high temperature for melting the slag. The composition of the slags was within the following limits: Silica, 19 to 23 per cent.; alumina, 5 to 8 per cent.; iron oxide, 2 to 3 per cent.; lime, 63 to 67 per cent.; magnesia, 2 to 4 per cent.; sulphur trioxide, 1.5 to 2.5 per cent. The slags were granulated with water and air, and also cooled slowly. Strengths equal to good high-strength Portland cement were obtained with some of the slags in spite of the unavoidable presence of a certain amount of calcium carbide. It appears that if the presence of carbide can be avoided greater strengths should be obtained for melted Portland cement prepared in a blastfurnace than for the same composition sintered. The problem of the commercial production of Portland cement in a blastfurnace has yet to be solved. The chief difficulties in the way of a solution are the presence of carbide in the finished clinker, the loss of heat in the molten slag, and the regulation of the setting time.

Physical and Chemical Influences on the Shrinkage of Portland Cement. By H. Kühl and D. Hsien. (Tonind. Zeit., 1935, pp. 843, 864, 913, 1016, 1028).—The authors have studied the shrinkage of thirteen cements of a wide range of compositions with and without additions of gypsum and calcium chloride and under widely differing conditions. The paper reviews the work done in this direction, and the authors find that in most cases their results confirm much of the work carried out by others; in a few instances, however, they diverge somewhat. It was found that long storage of cement before use considerably reduced shrinkage, even when the specimens were cured in perfectly dry air. A high water content reduced initial shrinkage, but increased final shrinkage. Shrinkage in air is greater with dry air, but with humidities between o and 40 per cent. it is practically constant. There is very little shrinkage in saturated air. Although a considerable reduction in early shrinkage could be obtained by keeping the specimens damp for a long time this did not reduce final shrinkage. The effect of chemical composition on shrinkage was investigated, and it was found that the silica content had no marked effect but that a high alumina ratio considerably increased it. The lowest shrinkage was obtained with cements of the Ferrari type which have equivalent amounts of alumina and iron oxide; this has been attributed to the low shrinkage of brownmillerite. Cements with a low lime content have small initial shrinkage, but considerable differences in the lime content have only a small effect on the final shrinkage. Shrinkage can be reduced by using the correct amount of gypsum, i.e., the amount of gypsum required for regulating the setting time to the usual period. Additions of calcium chloride increase both the swelling of the cement in water and the shrinkage in air.

Heat Evolution in the Synthesis of Portland Cement.

By O. F. HONUS.

A PAPER published in Zement (1935, pp. 761, 793, 823; 1936, p. 33) describes a study of the process of the reactions occurring in the formation of the constituents of Portland cement. The methods of calculating the heat changes during a reaction are set out, and the following are some of the results obtained.

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MONOCALCIUM FERRITE :--
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 $CaSO_4 + Fe_2O_3$ (cryst.) \rightleftharpoons $CaO.Fe_2O_3 + SO_2 + 0.5.O_2 - 95.952 kg. cal.$

 $[Ca] + [S] + 2[O_2] \rightarrow [CaSO_4] + 317.4 \text{ kg. cal.}$

 $2[Fe] + 1.5[O_2] \rightarrow [Fe_2O_3] \text{ crys.} + 195.19 \text{ kg. cal.}$

 $[S] + [O_2] \rightarrow [SO_2] + 71.1 \text{ kg. cal.}$

 $[Ca] + 2[Fe] + 2[O_2] = [CaFe_2O_4] + 345.54 \text{ kg. cal.}$

 $[CaO] + [Fe₂O₃] crys. \rightarrow [CaO.Fe₂O₃] + 18.85 kg. cal.$

 $[CaCO_3]$ spar + $[Fe_2O_3] \rightarrow [CaO.Fe_2O_3] + [CO_2] - 23.43$ kg. cal.

 $[CaCO_3]$ spar \rightarrow $[CaO] + [CO_2] - 42.28$ kg. cal.

MONOCALCIUM ALUMINATE :--

 $CaSO_4 + \gamma - Al_2O_3 \Longrightarrow Al_2O_3.CaO + SO_2 + 0.5 O_2$

- 98.182 + 0.051 kg. cal.

Ca + S = CaS + 90.8 kg. cal.

 $CaS + 2O_2 = CaSO_4 + 226.6$ kg. cal.

Ca + O = CaO + 131.5 kg. cal.

 $SO_2 + O = SO_3 + 20.9$ kg. cal.

 $CaO + SO_3 = CaSO_4 + 93.9$ kg. cal.

 $Ca + 2Al + 2O_2 = CaAl_2O_4 + 528.32$ kg. cal.

 $CaO + \gamma - Al_2O_3 = CaO.Al_2O_3 + 16.62 \text{ kg. cal.}$

Cao + y-111203 - Cao.111203 + 10.02 kg. cai.

CaCO₃ (aragonite) $+ \gamma$ -Al₂O₃ = CaO.Al₂O₃ + CO₂ - 25.96 kg. cal. CaCO₃ (spar) $+ \gamma$ -Al₂O₃ = CaO.Al₂O₃ + CO₂ - 25.66 kg. cal.

 $CaCO_3$ (precip.) + γ -Al₂O₃ = CaO.Al₂O₃ + CO₂ - 24.26 kg. cal.

If α -Al₂O₃ is used instead of γ -Al₂O₃ in the last three reactions the heats of reaction are — 39.06, — 38.76, and — 37.36 kg. cal. respectively.

MONOMAGNESIUM SILICATE:-

 $MgSO_4 + SiO_2 \Longrightarrow MgSiO_3 + SO_2 + 0.5 O_2 - 75.73 \text{ kg. cal.}$

Mg + O = MgO + 145.8 kg. cal.

 $MgO + SiO_2$ (crys.) = $MgSiO_3 + 9.68$ kg. cal.

 $MgO + SiO_2$ (amorph.) = $MgSiO_3 + 13.18$ kg. cal.

 $Mg + Si + 1.5 O_2 = MgSiO_3 + 359.48 kg. cal.$

 $MgCO_3$ (precip.) + SiO_2 (crys.) = $MgSiO_3 + CO_2 - 14.4$ kg. cal.

 $MgCO_3$ (precip.) + SiO_2 (amorph.) = $MgSiO_3 + CO_2 - 10.9$ kg. cal.

GEHLENITE :-

 $Al_2O_3.2SiO_2 + 3CaSO_4 \Longrightarrow Ca_3Al_2Si_2O_{10} + 2SO_3 + SO_2$

 $+ 0.5 O_2 - 251.22 \pm 0.12$ kg. cal.

 $_3$ CaSO₄ \implies $_3$ CaO + $_2$ SO₃ + SO₂ + 0.5 O₂ - 305.73 kg. cal.

$$3\text{CaSO}_4 + \text{Al}_2\text{O}_3.2\text{SiO}_2 \Longrightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 2\text{SO}_3 + \text{SO}_2 \\ + 0.5 \text{ O}_2 - 25\text{I}.22 \text{ kg. cal.} \\ 3[\text{CaO}] + [\text{Al}_2\text{O}_3.2\text{SiO}_2] \Rightarrow [\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10}] + 54.5\text{I kg. cal.} \\ \text{Al}_2\text{O}_3.2\text{SiO}_2 \text{ (metakaolin)} \Rightarrow \alpha\text{-Al}_2\text{O}_3 + 2\text{SiO}_2 + 28.2 \text{ kg. cal.} \\ \text{Al}_2\text{O}_3.2\text{SiO}_2 \text{ (metakaolin)} \Rightarrow \gamma\text{-Al}_2\text{O}_3 + 2\text{SiO}_2 \text{ (amorph.)} + 15.8 \text{ kg. cal.} \\ 2\text{SiO}_2 \text{ (amorph.)} \Rightarrow 2\text{SiO}_2 \text{ (crys.)} + 7.0 \text{ kg. cal.} \\ 2\text{SiO}_2 \text{ (amorph.)} \Rightarrow 2\text{SiO}_2 \text{ (cristobalite)} + 3.38 \text{ kg. cal.} \\ 3\text{CaO}_2 \text{ (quartz)} \Rightarrow 2\text{SiO}_2 \text{ (cristobalite)} + 3.38 \text{ kg. cal.} \\ 3\text{CaO} \Rightarrow \alpha\text{-Al}_2\text{O}_3 + 2\text{SiO}_2 \text{ (crist.)} + 38.68 \text{ kg. cal.} \\ 3\text{CaO} \Rightarrow 4\text{Al}_2\text{O}_3.2\text{SiO}_2 \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 54.5\text{I kg. cal.} \\ 3\text{CaO} \Rightarrow \gamma\text{-Al}_2\text{O}_3 + 2\text{SiO}_2 \text{ (amorph.)} \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 45.7\text{I kg. cal.} \\ 3\text{CaO} \Rightarrow \gamma\text{-Al}_2\text{O}_3 + 2\text{SiO}_2 \text{ (quartz)} \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 38.7\text{I kg. cal.} \\ 3\text{CaO} \Rightarrow \alpha\text{-Al}_2\text{O}_3 + 2\text{SiO}_2 \text{ (quartz)} \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 26.2\text{I kg. cal.} \\ 3\text{CaCO}_3 \text{ (spar)} + \text{Al}_2\text{Si}_2\text{O}_7 \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 72.23 \text{ kg. cal.} \\ 3\text{CaCO}_3 \text{ (spar)} + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 \text{ (quartz)} \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.} \\ \Rightarrow \text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10} + 3\text{CO}_2 - 88.13 \text{ kg. cal.}$$

Trade Notice.

CARBON AND ALLOY STEELS.—Messrs. Thos. Firth & John Brown, Ltd., of Sheffield, have issued a brochure giving data relating to their principal carbon and alloy steels, including typical analyses, heat treatment, mechanical and other features, applications, etc. The information is tabulated so that the most suitable steel for any purpose can be readily selected.

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